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(54) Fluorescent substances for vacuum ultraviolet radiation excited light-emitting devices

(57) A fluorescent substance for vacuum ultraviolet radiation excited light-emitting devices which emits light with a high luminance and is subject to only a small decrease in luminance due to exposure to plasma or the like, and a vacuum ultraviolet radiation excited light-emitting device including the fluorescent substance, are provided by way of a fluorescent substance for vacuum ultraviolet radiation excited light-emitting devices including: a compound represented by the general formula:  $mM^1O \cdot nM^2O \cdot 2M^3O_2$ , wherein  $M^1$  is at least one met-

al selected from Ca, Sr and Ba,  $M^2$  is at least one metal selected from Mg and Zn,  $M^3$  is at least one metal selected from Si and Ge, and  $m$  and  $n$  satisfy  $0.5 \leq m \leq 3.5$  and  $0.5 \leq n \leq 2.5$ , respectively, provided that when  $m=n=1$ ,  $M^1$  is either at least two metals selected from Ca, Sr and Ba or one of Sr and Ba; and at least one metal selected from Eu and Mn as an activator, and a vacuum ultraviolet radiation excited-light-emitting device including the fluorescent substance.

**Description**

**[0001]** The present invention relates to fluorescent substances suitably used for vacuum ultraviolet radiation excited light-emitting devices such as plasma display panels (hereinafter referred to as "PDPs") and rare gas lamps.

**[0002]** Fluorescent substances that emit light when excited with e.g. vacuum ultraviolet radiation include, for example, BaMgAl<sub>10</sub>O<sub>17</sub>:Eu comprising Ba, Mg, Al, O and an activator (Eu) as a blue fluorescent substance for vacuum ultraviolet radiation excited light-emitting devices, and Zn<sub>2</sub>SiO<sub>4</sub>:Mn comprising Zn, Si, O and an activator (Mn) as a green fluorescent substance. As well, (Y,Gd)BO<sub>3</sub>:Eu comprising Y, Gd, B, O and an activator (Eu), for example, has been known as a red fluorescent substance. Such fluorescent substances are also used in rare gas lamps. These prior art fluorescent substances for vacuum ultraviolet radiation excited light-emitting devices, however, are desired to exhibit further enhanced luminance.

**[0003]** In vacuum ultraviolet radiation excited light-emitting devices such as PDPs and rare gas lamps, causing discharge in a rare gas generates plasma and then, vacuum ultraviolet radiation is generated. The prior art fluorescent substances involve a problem that the luminance thereof decreases as they are exposed to plasma. Thus, there is a desire for a fluorescent substance for vacuum ultraviolet radiation excited light-emitting devices of which luminance does not much decrease due to exposure to plasma.

**[0004]** US-A-5,839,718 discloses a silicate fluorescent substance comprising a compound represented by the general formula: m(Sr<sub>1-a</sub>M<sup>1</sup><sub>a</sub>)O·n(Mg<sub>1-b</sub>M<sup>2</sup><sub>b</sub>)O·2(Si<sub>1-c</sub>Ge<sub>c</sub>)O<sub>2</sub>:Eu<sub>x</sub>Ln<sub>y</sub>, wherein M<sup>1</sup> is Ba, M<sup>2</sup> is at least one element selected from the group consisting of Be, Zn and Cd, Ln is at least one element selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, B, Al, Ga, In, Tl, Sb, Bi, As, P, Sn, Pb, Ti, Zr, Hf, V, Nb, Ta, Mo, W, Cr and Mn. Specific examples of such silicate fluorescent substances disclosed include Sr<sub>1.995</sub>MgSi<sub>2</sub>O<sub>7</sub>:Eu<sub>0.005</sub>, Dy<sub>0.025</sub>, Cl<sub>0.025</sub>, and Sr<sub>0.445</sub>Ba<sub>1.55</sub>MgSi<sub>2</sub>O<sub>7</sub>:Eu<sub>0.005</sub>, Dy<sub>0.025</sub>, Cl<sub>0.025</sub>. These fluorescent substances are for use as light accumulators for display in dark places or for similar purposes. "Extended abstracts of the sixth international conference on the science and technology of display phosphors", pages 21-24, discloses CaMgSi<sub>2</sub>O<sub>6</sub>:Eu as a fluorescent substance for vacuum ultraviolet radiation excited light-emitting devices.

**[0005]** Such fluorescent substances comprising silicate still have the problem that their luminance is insufficient and decreases due to exposure to plasma.

**[0006]** It is an object of the present invention to provide a fluorescent substance for vacuum ultraviolet radiation excited light-emitting devices which emits light with a higher luminance and a small decrease in luminance after the exposure to plasma.

**[0007]** This object could be achieved on the basis of the finding that, among silicate or germanate fluorescent substances for vacuum ultraviolet radiation excited light-emitting devices, a fluorescent substance having a specific composition comprising: a compound represented by the general formula, mM<sup>1</sup>O·nM<sup>2</sup>O·2M<sup>3</sup>O<sub>2</sub>, wherein M<sup>1</sup> is at least one metal selected from Ca, Sr and Ba, M<sup>2</sup> is at least one metal selected from Mg and Zn, M<sup>3</sup> is at least one metal selected from Si and Ge, and m and n satisfy 0.5≤m≤3.5 and 0.5≤n≤2.5, respectively, provided that when m=n=1, M<sup>1</sup> is either at least two metals selected from Ca, Sr and Ba, or one of Sr and Ba; and at least one metal selected from Eu and Mn as an activator, emits light with a higher luminance and a smaller decrease in luminance after the exposure to plasma.

**[0008]** Accordingly, the present invention provides a fluorescent substance for vacuum ultraviolet radiation excited light-emitting devices, comprising: a compound represented by the general formula, mM<sup>1</sup>O·nM<sup>2</sup>O·2M<sup>3</sup>O<sub>2</sub>, wherein M<sup>1</sup> is at least one metal selected from Ca, Sr and Ba, M<sup>2</sup> is at least one metal selected from Mg and Zn, M<sup>3</sup> is at least one metal selected from Si and Ge, and m and n satisfy 0.5≤m≤3.5 and 0.5≤n≤2.5, respectively, provided that when m=n=1, M<sup>1</sup> is either at least two metals selected from Ca, Sr and Ba, or one of Sr and Ba; and at least one metal selected from Eu and Mn as an activator, emits light with a higher luminance and a smaller decrease in luminance after the exposure to plasma.

**[0009]** The fluorescent substance for vacuum ultraviolet radiation excited light-emitting devices according to the present invention is characterized by comprising: a base crystal formed of a compound represented by the general formula: mM<sup>1</sup>O·nM<sup>2</sup>O·2M<sup>3</sup>O<sub>2</sub>, wherein M<sup>1</sup> is at least one metal selected from Ca, Sr and Ba, M<sup>2</sup> is at least one metal selected from Mg and Zn, M<sup>3</sup> is at least one metal selected from Si and Ge, and m and n satisfy 0.5≤m≤3.5 and 0.5≤n≤2.5, respectively, provided that when m=n=1, M<sup>1</sup> is either at least two metals selected from Ca, Sr and Ba, or one of Sr and Ba; and at least one metal selected from Eu and Mn as an activator. The present invention also provides a vacuum ultraviolet radiation excited light-emitting device comprising the fluorescent substance defined above.

**[0010]** When m=n=1 in the above-noted general formula, M<sup>1</sup> is selected from Sr, Ba, the combination of Sr, Ba and Ca, combination of Sr and Ca, combination of Ba and Sr, and combination of Ba and Ca.

**[0011]** Preferably, the fluorescent substance for vacuum ultraviolet radiation excited light-emitting devices according to the present invention has a crystal structure as same as diopside, akermanite, or merwinite.

**[0012]** Among fluorescent substances having the same crystal structure as diopside, one comprising a compound of the above-noted general formula where m=n=1 is preferable. A more preferable one as a fluorescent substance for vacuum ultraviolet radiation excited light-emitting devices is of a composition in which M<sup>1</sup> and M<sup>2</sup> are partially replaced with the activators Eu

and Mn, respectively and which is represented by the general formula:  $(M^1_{1-a}Eu_a)(M^2_{1-b}Mn_b)M^3_2O_6$ , wherein M<sup>1</sup> is either at least two metals selected from Ca, Sr and Ba, or one of Sr and Ba, M<sup>2</sup> is at least one metal selected from Mg and Zn, M<sup>3</sup> is at least one metal selected from Si and Ge, and a and b satisfy  $0 \leq a \leq 0.5$ ,  $0 \leq b \leq 0.5$ , and  $0 < a+b$ .

[0013] A still preferred one of fluorescent substances having the same crystal structure as diopside and comprising a compound of the above-noted general formula where m=n=1 has a composition in which M<sup>1</sup> is Ca and Sr, M<sup>2</sup> and M<sup>3</sup> are Mg and Si, respectively, and Ca is partially replaced with the activator Eu and which is represented by the general formula:  $Ca_{1-c-d}Sr_cEu_dMgSi_2O_6$ , wherein c and d satisfy  $0 < c \leq 0.1$  and  $0 < d \leq 0.1$ , respectively.

[0014] Among fluorescent substances having the same crystal structure as akermanite, one comprising a compound of the above-noted general formula where m=2 and n=1 is preferable. A more preferable one as a fluorescent substance for vacuum ultraviolet radiation excited light-emitting devices has a composition in which M<sup>1</sup> and M<sup>2</sup> are partially replaced with the activators Eu and Mn, respectively and which is represented by the general formula:  $(M^1_{1-e}Eu_e)_2(M^2_{1-f}Mn_f)M^3_2O_7$ , wherein M<sup>1</sup> is at least one metal selected from Ca, Sr and Ba, M<sup>2</sup> is at least one metal selected from Mg and Zn, M<sup>3</sup> is at least one metal selected from Si and Ge, and e and f satisfy  $0 \leq e \leq 0.5$ ,  $0 \leq f \leq 0.5$ , and  $0 < e+f$ . Still more preferable is a fluorescent substance having a composition in which f=0, and M<sup>3</sup> is Si and which is represented by the general formula:  $(M^1_{1-e}Eu_e)_2M^2_2Si_2O_7$ , wherein M<sup>1</sup> is at least one metal selected from Ca, Sr and Ba, M<sup>2</sup> is at least one metal selected from Mg and Zn, and e satisfies  $0.001 \leq e \leq 0.1$ .

[0015] Among fluorescent substances having the same crystal structure as akermanite, one comprising a compound of the above-noted general formula where m=1 and n=2 is preferable. A more preferable one as a fluorescent substance for vacuum ultraviolet radiation excited light-emitting devices has a composition in which M<sup>1</sup> and M<sup>2</sup> are partially replaced with the activators Eu and Mn, respectively and which is represented by the general formula:  $(M^1_{1-h}Eu_h)(M^2_{1-i}Mn_i)_2M^3_2O_7$ , wherein M<sup>1</sup> is at least one metal selected from Ca, Sr and Ba, M<sup>2</sup> is at least one metal selected from Mg and Zn, M<sup>3</sup> is at least one metal selected from Si and Ge, and h and i satisfy  $0 \leq h \leq 0.5$ ,  $0 \leq i \leq 0.5$ , and  $0 < h+i$ .

[0016] Among fluorescent substances having the same crystal structure as merwinite, one comprising a compound of the above-noted general formula where m=3 and n=1 is preferable. A more preferable one as a fluorescent substance for vacuum ultraviolet radiation excited light-emitting devices has a composition in which M<sup>1</sup> and M<sup>2</sup> are partially replaced with the activators Eu and Mn, respectively and which is represented by the general formula:  $(M^1_{1-j}Eu_j)_3(M^2_{1-k}Mn_k)M^3_2O_8$ , wherein M<sup>1</sup> is at least one metal selected from Ca, Sr

and Ba, M<sup>2</sup> is at least one metal selected from Mg and Zn, M<sup>3</sup> is at least one metal selected from Si and Ge, and j and k satisfy  $0 \leq j \leq 0.5$ ,  $0 \leq k \leq 0.5$ , and  $0 < j+k$ .

5 [0017] Among fluorescent substances having the same crystal structure as diopside, akermanite or merwinite, those having the same crystal structure as diopside and those having the same crystal structure as merwinite are preferable. Fluorescent substances having 10 the same structure as diopside are particularly preferable.

[0018] Raw materials usable as calcium, strontium and barium sources in the preparation of the fluorescent substance of the present invention may be either those 15 which can be decomposed into oxides at high temperatures such as hydroxides, carbonates, nitrates, halides and oxalates of calcium, strontium and barium having high purity (99% or more), or oxides of calcium, strontium and barium having high purity (99.9% or more).

[0019] Raw materials usable as magnesium and zinc sources may be either those which can be decomposed into oxides at high temperatures such as hydroxides, carbonates, nitrates, halides and oxalates of magnesium and zinc having high purity (99% or more), or oxides 20 of magnesium and zinc having high purity (99% or more).

[0020] Raw materials usable as silicon and germanium sources may be either those which can be decomposed into oxides at high temperatures such as hydroxides, carbonates, nitrates, halides, and oxalates of silicon and germanium having high purity (99% or more), or oxides of silicon and germanium having high purity (99% or more).

[0021] Raw materials containing europium or manganese that will serve as an activator may be either those 35 which can be decomposed into oxides at high temperatures such as hydroxides, carbonates, nitrates, halides and oxalates of europium and manganese having high purity (99% or more), or oxides of europium and manganese having high purity (99% or more).

[0022] There is no particular limitation to the method 40 of preparing the fluorescent substance of the present invention. The fluorescent substance may be prepared, for example, by mixing the aforementioned raw materials and calcining the mixture.

[0023] For instance, the fluorescent substance having the composition represented by the formula:  $(M^1_{1-a}Eu_a)(M^2_{1-b}Mn_b)M^3_2O_6$ , which is one of the preferable compositions described above, can be prepared by weighing 50 and blending the foregoing raw materials into a predetermined composition, mixing them and calcining the mixture. In mixing such raw materials, it is possible to use e.g. a ball mill, V-Type mixer or stirring device.

[0024] After the mixing, the mixture is calcined at a temperature, for example, ranging between about 1000°C and about 1500°C for about 1 to about 100 hours, to give the fluorescent substance of the present invention. In the case where those raw materials which 55

can be decomposed into oxides at high temperatures such as hydroxides, carbonates, nitrates, halides and oxalates of the necessary elements are used, it is possible to conduct pre-calcination of the mixture at a temperature, for example, ranging between about 600°C and about 900°C prior to the main-calcination.

**[0025]** There is no particular limitation to the calcining atmosphere, but calcining in a reducing atmosphere comprising, for example, nitrogen or argon and hydrogen in an amount of 10% by volume is preferable. The pre-calcination may be performed either in atmospheric air or in a reducing atmosphere. To promote the calcining reaction, an appropriate amount of a flux may be added.

**[0026]** Further, the fluorescent substance obtained by the above-described method may be pulverized using, for example, a ball mill or jet mill. Further, the substance may be washed and classified. To obtain a fluorescent substance of higher crystallinity, re-calcination may be performed.

**[0027]** The fluorescent substance of the present invention thus obtained is capable of emitting light with a high luminance when excited with vacuum ultraviolet radiation and exhibits only a small decrease in luminance due to exposure to plasma. In the manufacture of e.g. a PDP or rare gas lamp, a process typically includes dispersing the fluorescent substance in a solvent, adding a binder to the dispersion liquid, applying the dispersion liquid onto a light-emitting section, and heating the dispersion liquid thus applied to about 500°C to remove the binder. The fluorescent substance of the present invention, even if subjected to such a process, exhibits only a small decrease in luminance due to the heat treatment. Accordingly, use of the fluorescent substance of the present invention in a vacuum ultraviolet radiation excited light-emitting device such as PDP or rare gas lamp makes it possible to realize a PDP or rare gas lamp exhibiting a high luminance and a prolonged service life. Hence, the fluorescent substance of the present invention is suitable for vacuum ultraviolet radiation excited light-emitting devices.

**[0028]** The fluorescent substance of the present invention can also be excited with ultraviolet radiation out of the vacuum ultraviolet region, x-rays or electron beam and hence may be employed in devices using ultraviolet radiation out of the vacuum ultraviolet region, X-rays or electron beam as an excitation source.

#### EXAMPLES

**[0029]** The present invention is in more detailed with reference to the following examples, but the invention is not limited to those examples.

#### EXAMPLE 1

**[0030]** Raw materials, namely, calcium carbonate ( $\text{CaCO}_3$  produced by WAKOJUNYAKU CO., LTD.),

strontium carbonate ( $\text{SrCO}_3$  produced by WAKOJUNYAKU CO., LTD.), europium oxide ( $\text{Eu}_2\text{O}_3$  produced by SHINETSU KAGAKUKOGYO CO., LTD.), basic magnesium carbonate ( $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$  produced by WAKOJUNYAKU CO., LTD.) and silicon oxide ( $\text{SiO}_2$  produced by WAKOJUNYAKU CO., LTD.), were weighed and mixed together so that the molar ratio of  $\text{CaCO}_3:\text{SrCO}_3:\text{Eu}_2\text{O}_3:((\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}):\text{SiO}_2$  was 0.9215:0.0485:0.015:0.2:2. The resulting mixture

was calcined at 1200°C for two hours in a stream of Ar gas containing  $\text{H}_2$  in an amount of 2% by volume, then ground, and again calcined at 1200°C for two hours in a stream of Ar gas containing  $\text{H}_2$  in an amount of 2% by volume. A fluorescent substance of a composition represented by the formula:

$\text{Ca}_{0.9215}\text{Sr}_{0.0485}\text{Eu}_{0.015}\text{MgSi}_2\text{O}_6$  was thus obtained. When this fluorescent substance was irradiated with ultraviolet radiation using an excimer 146-nm lamp (Model: H0012 manufactured by USHIO DENKI CO.) in a

vacuum chamber under a pressure of 6.7 Pa ( $5 \times 10^{-2}$  Torr) or lower, it emitted blue light with a luminance of 24 cd/m<sup>2</sup>.

**[0031]** The fluorescent substance thus obtained was subjected to a heat treatment at 500°C for 30 minutes

in air. The fluorescent substance having undergone the heat treatment was measured for its luminance and, as a result, there was no decrease in luminance as compared with the luminance of the fluorescent substance before the heat treatment.

**[0032]** The fluorescent substance obtained was placed in a gas atmosphere having a Xe Ne composition ratio of 5% 95% by volume under a pressure of 13.2 Pa and exposed to plasma of 10 W for 30 minutes, then to plasma of 50 W for 15 minutes. After the exposure to plasma, the fluorescent substance was measured for its luminance and, as a result, there was no decrease in luminance as compared with the luminance of the fluorescent substance before the exposure to plasma.

**[0033]** The fluorescent substance obtained was subjected to a heat treatment at 500°C for 30 minutes in air. Subsequently, the fluorescent substance was placed in a gas atmosphere having a Xe Ne composition ratio of 5% 95% by volume under a pressure of 13.2 Pa and exposed to plasma of 10 W for 30 minutes, then to plasma of 50 W for 15 minutes. After the exposure to plasma,

the fluorescent substance was measured for its luminance and, as a result, there was a decrease as small as 4% in luminance as compared with the luminance of the fluorescent substance before the heat treatment and the exposure to plasma.

#### EXAMPLE 2

**[0034]** Raw materials, namely, strontium carbonate ( $\text{SrCO}_3$  produced by WAKOJUNYAKU CO., LTD.), barium carbonate ( $\text{BaCO}_3$  produced by WAKOJUNYAKU CO., LTD.), europium oxide ( $\text{Eu}_2\text{O}_3$  produced by SHINETSU KAGAKUKOGYO CO., LTD.), basic magnesi-

um carbonate ( $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$  produced by WAKOJUNYAKU CO., LTD.) and silicon oxide ( $\text{SiO}_2$  produced by WAKOJUNYAKU CO., LTD.), were weighed and mixed together so that the molar ratio of  $\text{SrCO}_3:\text{BaCO}_3:\text{Eu}_2\text{O}_3:(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}:\text{SiO}_2$  was 2.28:0.57:0.075:0.2:2. The resulting mixture was calcined at 1200°C for two hours in a stream of Ar gas containing  $\text{H}_2$  in an amount of 2% by volume. A fluorescent substance having a composition represented by the formula:  $\text{Sr}_{2.28}\text{Ba}_{0.57}\text{Eu}_{0.15}\text{MgSi}_2\text{O}_8$  was thus obtained. When this fluorescent substance was irradiated with ultraviolet radiation using an excimer 146-nm lamp (Model: H0012 manufactured by USHIO DENKI CO.) in a vacuum chamber under a pressure of 6.7 Pa ( $5 \times 10^{-2}$  Torr) or lower, it emitted blue light with a luminance of 30 cd/m<sup>2</sup>.

#### EXAMPLE 3

**[0035]** Raw materials, namely, barium carbonate ( $\text{BaCO}_3$  produced by KANTOKAGAKU CO, LTD.), europium oxide ( $\text{Eu}_2\text{O}_3$  produced by SHINETSU KAGAKU-KOGYO CO., LTD.), magnesium oxide ( $\text{MgO}$  produced by KANTOKAGAKU CO., LTD.) and silicon oxide ( $\text{SiO}_2$  produced by KOJUNDOKAGAKU KENKYUSHO CO., LTD.), were weighed and mixed together so that the molar ratio of  $\text{BaCO}_3:\text{Eu}_2\text{O}_3:\text{MgO}:\text{SiO}_2$  was 1.98:0.01:1:2. 0.1 mol of  $\text{B}_2\text{O}_3$  as a flux was added relative to 1 mol of the product, and the resulting mixture was sufficiently wet-blended in acetone with mortar, followed by drying. The mixed raw material thus obtained was put into a stainless steel mold and then pressurized at 40 Mpa to form a circular pellet having a size of 15 mm (diameter) x 3 mm (thickness). The resulting pellet was put into an alumina crucible and calcined at 1200°C for three hours in an atmosphere having a  $\text{H}_2$  Ar composition ratio of 5% 95% by volume. A fluorescent substance having a composition represented by the formula:  $\text{Ba}_{1.98}\text{Eu}_{0.02}\text{MgSi}_2\text{O}_7$  was thus obtained. When this fluorescent substance was irradiated with ultraviolet radiation using an excimer 146-nm lamp (Model: H0012 manufactured by USHIO DENKI CO.) in a vacuum chamber under a pressure of 6.7 Pa ( $5 \times 10^{-2}$  Torr) or lower, it emitted green light with a luminance of 95 cd/m<sup>2</sup>.

#### EXAMPLE 4

**[0036]** Used as starting materials for the preparation of  $(\text{Sr}_{0.99}\text{Eu}_{0.01})_2\text{MgSi}_2\text{O}_7$  were strontium carbonate ( $\text{SrCO}_3$  produced by KANTOKAGAKU CO, LTD.), europium oxide ( $\text{Eu}_2\text{O}_3$  produced by SHINETSU KAGAKU-KOGYO CO., LTD.), magnesium oxide ( $\text{MgO}$  produced by KANTOKAGAKU CO., LTD.) and silicon oxide ( $\text{SiO}_2$  produced by KOJUNDOKAGAKU KENKYUSHO CO., LTD.). These materials were weighed and mixed together so that the molar ratio of  $\text{SrCO}_3:\text{Eu}_2\text{O}_3:\text{MgO}:\text{SiO}_2$  was 1.98:0.01:1:2, then 0.1 mol of  $\text{B}_2\text{O}_3$  as a flux was

added relative to 1 mol of the product, i.e.,  $(\text{Sr}_{0.99}\text{Eu}_{0.01})_2\text{MgSi}_2\text{O}_7$ , and the resulting mixture was sufficiently wet-blended in acetone with mortar, followed by drying. The mixed raw material thus obtained was put into a stainless steel mold and then pressurized at 40 Mpa to form a circular pellet having a size of 15 mm (diameter) x 3 mm (thickness). The resulting pellet was put into an alumina crucible and calcined at 1200°C for three hours in an atmosphere having a  $\text{H}_2$  Ar composition ratio of 5% 95%. When the sample resulting from the calcining was irradiated with ultraviolet radiation having a wavelength of 254 nm or 365 nm, it emitted light blue light with a high luminance in either case. When the sample was irradiated with ultraviolet radiation using an excimer 146-nm lamp (manufactured by USHIO DENKI CO.) in a vacuum chamber under a pressure of 6.7 Pa ( $5 \times 10^{-2}$  Torr) or lower, it emitted intensive light blue light with a luminance of 25 cd/m<sup>2</sup>.

#### EXAMPLE 5

**[0037]** Used as starting materials for the preparation of  $(\text{Sr}_{0.99}\text{Eu}_{0.01})_2\text{ZnSi}_2\text{O}_7$  were strontium carbonate ( $\text{SrCO}_3$ ), europium oxide ( $\text{Eu}_2\text{O}_3$ ), zinc oxide ( $\text{ZnO}$ ) and silicon oxide ( $\text{SiO}_2$ ). These materials were weighed and mixed together so that the molar ratio of  $\text{SrCO}_3:\text{Eu}_2\text{O}_3:\text{ZnO}:\text{SiO}_2$  was 1.98:0.01:1:2, then 0.1 mol of  $\text{B}_2\text{O}_3$  as a flux was added relative to 1 mol of the product, i.e.,  $(\text{Sr}_{0.99}\text{Eu}_{0.01})_2\text{ZnSi}_2\text{O}_7$ , and the resulting mixture was sufficiently wet-blended in acetone with mortar, followed by drying. The mixed raw material thus obtained was put into a stainless steel mold and then pressurized at 40 Mpa to form a circular pellet having a size of 15 mm (diameter) x 3 mm (thickness). The resulting pellet was put into an alumina crucible and calcined at 1200°C for three hours in an atmosphere having a  $\text{H}_2$  Ar composition ratio of 5% 95%. When the sample resulting from the calcining was irradiated with ultraviolet radiation having a wavelength of 254 nm or 365 nm, it emitted bluish green light with a high luminance.

#### COMPARATIVE EXAMPLE 1

**[0038]** Raw materials, namely, calcium carbonate ( $\text{CaCO}_3$  produced by WAKOJUNYAKU CO, LTD.), europium oxide ( $\text{Eu}_2\text{O}_3$  produced by SHINETSU KAGAKU-KOGYO CO., LTD.), basic magnesium carbonate ( $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$  produced by WAKOJUNYAKU CO., LTD.) and silicon oxide ( $\text{SiO}_2$  produced by WAKOJUNYAKU CO., LTD.), were weighed and mixed together so that the molar ratio of  $\text{CaCO}_3:\text{Eu}_2\text{O}_3:(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}:\text{SiO}_2$  was 0.95:0.025:0.2:2. The resulting mixture was calcined at 1200°C for two hours in a stream of Ar gas containing  $\text{H}_2$  in an amount of 2% by volume. A fluorescent substance having a composition represented by the formula:  $\text{Ca}_{0.95}\text{Eu}_{0.05}\text{MgSi}_2\text{O}_6$  was thus obtained. When this fluorescent substance was irradiated with ultraviolet radia-

ation using an excimer 146-nm lamp (Model: H0012 manufactured by USHIO DENKI CO.) in a vacuum chamber under a pressure of 6.7 Pa ( $5 \times 10^{-2}$  Torr) or lower, it emitted blue light with a luminance of 12 cd/m<sup>2</sup>.

#### COMPARATIVE EXAMPLE 2

**[0039]** A commercially-available blue light emitting fluorescent substance ( $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ ) was subjected to a heat treatment at 500°C for 30 minutes in air. The fluorescent substance having undergone the heat treatment was measured for its luminance and, as a result, there was a 1% decrease in luminance as compared with the luminance of the fluorescent substance before the heat treatment.

**[0040]** The commercially-available blue light emitting fluorescent substance ( $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ ) was placed in a gas atmosphere having a Xe Ne composition ratio of 5% 95% by volume under a pressure of 13.2 Pa and exposed to plasma of 10 W for 30 minutes, then to plasma of 50 W for 15 minutes. After the exposure to plasma, the fluorescent substance was measured for its luminance and, as a result, there was a 25% decrease in luminance as compared with the luminance of the fluorescent substance before the exposure to plasma.

**[0041]** The commercially-available blue light emitting fluorescent substance ( $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ ) was subjected to a heat treatment at 500°C for 30 minutes in air. Subsequently, the fluorescent substance was placed in a gas atmosphere having a Xe Ne composition ratio of 5% 95% by volume under a pressure of 13.2 Pa and exposed to plasma of 10 W for 30 minutes, then to plasma of 50 W for 15 minutes. After the exposure to plasma, the fluorescent substance removed from the gas atmosphere was measured for its luminance and, as a result, there was a 28% decrease in luminance as compared with the luminance of the fluorescent substance in a state before undergoing the heat treatment and the exposure to plasma.

**[0042]** The fluorescent substance of the present invention emits light with a high luminance and exhibits only a small decrease in luminance due to exposure to plasma and, hence, is particularly suitable for use in vacuum ultraviolet radiation excited light-emitting devices such as PDPs and rare gas lamps. Since the fluorescent substance makes it possible to realize vacuum ultraviolet radiation excited light-emitting devices exhibiting high luminance, it is highly useful for industry.

5 one metal selected from Si and Ge, and m and n satisfy  $0.5 \leq m \leq 3.5$  and  $0.5 \leq n \leq 2.5$ , respectively, provided that when m=n=1, M<sup>1</sup> is either at least two metals selected from Ca, Sr and Ba, or one of Sr and Ba; and at least one metal selected from Eu and Mn as an activator.

10 2. The substance according to claim 1, which has the same crystal structure as diopside.

15 3. The substance according to claim 2, wherein m=n=1.

15 4. The substance according to claim 2, wherein M<sup>1</sup> is Ca and Sr, and M<sup>2</sup> and M<sup>3</sup> are Mg and Si, respectively and the activator is Eu.

20 5. The substance according to claim 4, which is of a composition represented by the formula:  $\text{Ca}_{1-c-d}\text{Sr}_c\text{Eu}_d\text{MgSi}_2\text{O}_6$ , wherein c and d  $0 < c \leq 0.1$  and  $0 < d \leq 0.1$ , respectively.

25 6. The substance according to claim 1, which has the same crystal structure as akermanite.

25 7. The substance according to claim 6, wherein m=2 and n=1.

30 8. The substance according to claim 6, wherein M<sup>3</sup> is Si and the activator is Eu.

35 9. The substance according to claim 6, wherein m=1 and n=2.

35 10. The substance according to claim 1, which has the same crystal structure as merwinite.

40 11. The substance according to claim 10, wherein m=3 and n=1.

45 12. A vacuum ultraviolet radiation excited light-emitting device comprising a fluorescent substance according to any one of claims 1 to 11.

#### Claims

1. A fluorescent substance for vacuum ultraviolet radiation excited light-emitting devices comprising: a compound represented by the general formula,  $m\text{M}^1\text{O} \cdot n\text{M}^2\text{O} \cdot 2\text{M}^3\text{O}_2$ , wherein M<sup>1</sup> is at least one metal selected from Ca, Sr and Ba, M<sup>2</sup> is at least one metal selected from Mg and Zn, M<sup>3</sup> is at least